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Charge transport in poly(p-phenylene vinylene) at low temperature and high electric field

I. Katsouras^{a,b,*}, A. Najafi^a, K. Asadi^c, A.J. Kronemeijer^d, A.J. Oostra^a, L.J.A. Koster^a, D.M. de Leeuw^{a,b,c}, P.W.M. Blom^{a,b}

^a Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

^b Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

^c Philips Research Laboratories, High Tech Campus 4, 5656AE Eindhoven, The Netherlands

^d Optoelectronics Group, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom

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ABSTRACT

Charge transport in poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV)-based hole-only diodes is investigated at high electric fields and low temperatures using a novel diode architecture. Charge carrier densities that are in the range of those in a field-effect transistor are achieved, bridging the gap in the mobility versus charge carrier density plot between polymer-based light-emitting diodes and field-effect transistors. The extended field range that is accessed allows us to discuss the applicability of current theoretical models of charge transport, using numerical simulations. Finally, within a simple approximation, we extract the hopping length for holes in MEH-PPV directly from the experimental data at high fields, and we derive a value of 1.0 ± 0.1 nm.

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1. Introduction

Understanding and modeling charge transport in conjugated polymers is crucial to optimize the performance of organic semiconductor devices such as light-emitting diodes (OLEDs), field-effect transistors (OFETs) and solar cells [1]. Charge carrier transport in these materials has been under intense research in the past decades. The workhorses for polymeric light-emitting diodes are derivatives of poly(p-phenylene vinylene) such as poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV). It has been shown that the transport of holes, which are the dominant charge carriers in this material, can be explained by a space-charge limited current (SCLC) [2], with a mobility originating from a hopping process between

localized sites in a Gaussian density of states (DOS) [3]. It has been demonstrated that the mobility depends on density, electric field, and temperature [4,5]. A commonly used model to describe the charge transport is the Extended Gaussian Disorder Model (EGDM) [6]. In this model the dependence of the mobility on carrier density governs the hole conduction at room temperature, whereas at low temperatures the field dependence dominates.

A general problem to experimentally validate charge transport models is that in conventional OLEDs the charge transport is measured only in a limited range of electric field and temperature. A typical example is presented in Fig. 1, where the experimental current density of an MEH-PPV hole-only diode at room temperature (symbols) is presented as a function of electric field. The transport is typically measured in a field range between 1 MV/m and 30 MV/m. We note that in a SCL diode the electric field and carrier density are inhomogeneous; in Fig. 1 we plot the average electric field V/L with V the applied voltage

* Corresponding author at: Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. Tel.: +49 6131 379 721.

E-mail addresses: katsouras@mpip-mainz.mpg.de, I.Katsouras@rug.nl (I. Katsouras).

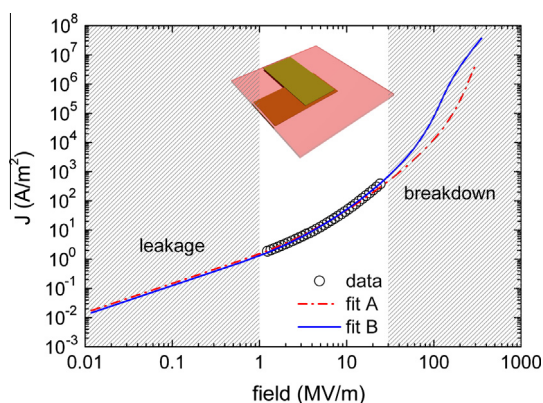


Fig. 1. Current density as a function of applied electric field for an MEH-PPV hole-only diode. Measurements were performed at room temperature at electric fields between 1 and 30 MV/m. The solid lines are fits to the data using a numerical drift–diffusion model based on the Extended Gaussian Disorder Model. The solid lines are calculated using two extreme values for the lattice constant of 1 nm (fit A) and 2 nm (fit B). Inset shows the standard layout of an organic light-emitting diode.

and L the thickness of the sample. The solid lines in Fig. 1 are simulations using a numerical drift–diffusion model to account for the inhomogeneous field and density [7]. In this simulation a field- and density dependent mobility based on the EGDM model has been employed. As an illustration of two extreme cases, the solid lines represent simulations where we have varied the lattice constant, i.e. 1 nm and 2 nm, keeping all other parameters fixed. It is observed that within the conventional characterization window of about 1–30 MV/m it is not possible to resolve which set of parameters best describes the experimental data. The two fits deviate but only at an inaccessible field range. An extension of the experimental measurement window is therefore required to truly validate charge transport models that have been proposed in recent years.

The shaded areas in Fig. 1 at higher and lower fields are not easily accessible with standard measurement techniques and device geometries. Extension to higher fields is hampered by dielectric breakdown under a continuous applied DC bias. At low electric fields reliable transport measurements are hampered by parasitic leakage currents that mask the diode current, especially at low temperatures, since the device current decreases much faster with temperature than the parasitic currents. Here we characterize hole-only diodes of MEH-PPV in an unprecedented voltage and temperature range, by employing a previously developed technology of molecular junctions [8]. The diodes are defined in a matrix of insulating photoresist, eliminating the problem of parasitic leakage. Small device areas allow for higher biases to be applied before the current reaches the critical level at which the diodes break down. The application of short voltage pulses further extends the applied electric field range up to a maximum of 300 MV/m [9]. The resulting high field and low temperature measurements on hole-only diodes of MEH-PPV are used to test the ability of existing theoretical models to describe charge carrier transport in MEH-PPV at high fields. We use the achieved high charge carrier densities to address the charge

carrier dependence of the mobility in the gap that exists between carrier densities in polymer-based light-emitting diodes and field-effect transistors. Finally, within a simple approximation we attempt to extract the hopping length directly from the experimental data at high fields.

2. Experimental

Molecular junctions were prepared as described previously [10] on a 6-in. Si monitor wafer with a 500 nm thermally grown SiO_2 passivation layer. A 60 nm Au bottom electrode was evaporated onto a Ti adhesion layer and patterned with I-line photolithography. Vertical interconnects (*vias*) ranging from 1 μm to 100 μm in diameter were defined in insulating photoresist by conventional spin coating and UV-lithography. The wafer was divided by laser cutting in identical 2×3 cm pieces, each containing 110 junctions. The amorphous polymer poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV), synthesized in our laboratory via the Gilch method [11], was dissolved in toluene and spincoated in ambient conditions. A solution with a concentration of 4.5 mg/ml yielded layers of 115 nm and 85 nm when spincoated at 1000 rpm and 2000 rpm, respectively. A layer of 40 nm was obtained from a solution with a concentration of 2.5 mg/ml, by spincoating at 3000 rpm. The final thickness was measured on reference layers spincoated on clean glass slides using a Dektak profilometer. Subsequently, the conducting polymer PEDOT:PSS, a water-based suspension of poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid), AGFA ICP 1020 (Agfa-Gevaert), was spincoated from a formulation containing the non-ionic Zonyl FSO-100 (DuPont) fluoro-surfactant. The conductivity amounted to 300 S/cm. The diodes were subsequently annealed for 1 h at 85 °C in dynamic vacuum. Finally, a 150 nm top gold contact was thermally evaporated through a shadow mask. This top contact is utilized as a self-aligned reactive ion etching mask for the removal of the redundant PEDOT:PSS. Stable and reproducible junctions were obtained.

DC and pulsed current measurements were performed in a cryogenic probe station (Janis Research Co.), using a Keithley 4200 Semiconductor Parameter Analyzer equipped with the Keithley Pulse Measurement Unit. The current through the junctions scaled with the lateral dimensions of the *vias* with only a small standard deviation. The transport of the diodes could be measured with DC biases between 1 mV and about 10 V, depending on the layer thickness. To circumvent electrical breakdown at higher DC bias, pulse measurements were applied [9]. The pulse width was set at 500 μs with a rise and fall time of 1 μs . At low temperature and with a low duty cycle of 10% the transport could be measured up to high biases of 13 V, 30 V and 40 V for the diodes with thickness of 40 nm, 85 nm and 115 nm respectively.

3. Charge transport measurements and modeling

The current density as a function of electric field for MEH-PPV hole-only diodes, fabricated in the molecular

junction architecture with MEH-PPV layer thicknesses of 40 nm, 85 nm and 115 nm, are presented in Fig. 2a–c. The schematic diode layout showing the difference to a conventional OLED geometry is shown in Fig. 2d. The temperature was varied between 150 K and 300 K. The electrical transport could be measured over an electric field range of about 5 decades, from 0.01 MV/m up to 300 MV/m. The transport characteristics were nearly symmetric for negative and positive bias, showing that the highest occupied molecular orbital (HOMO) of the MEH-PPV layer is well aligned with the HOMO of the PEDOT:PSS top electrode and with the Fermi level of the bottom gold contact. The transport is Ohmic at low fields. Subsequently, with increasing field, a quadratic dependence of the device current on the voltage is observed indicating a space-charge limited (SCL) current, following Mott–Gurney's square law [12]. At even higher fields a deviation from the square-law dependence is observed. The deviation is due to the field and charge carrier density dependence of the mobility. At low bias the current density decreases with decreasing temperature. At higher fields the temperature dependence is weaker. At sufficiently high fields the temperature dependence disappears and the current density vs. electric field characteristics converge.

To describe the experimental data we used a numerical drift–diffusion model [7] with a mobility based on the

commonly used Extended Gaussian Disorder Model (EGDM) of Pasveer et al. [6]. This model takes into account the density and field dependence of the mobility [6]. The parameterization used by Pasveer et al. [6] is not valid for high charge-carrier densities, which are achieved in our thin layer diodes at high fields. We therefore performed numerical simulations using an improved parameterization, valid at high charge-carrier densities [13]. We chose a standard set of fitting parameters, previously used in literature to describe transport in MEH-PPV hole-only diodes [6,14]. Fig. 3 shows the fits of the experimental data for the MEH-PPV diodes with a layer thickness of 85 nm. A magnification of the high field regime is given in the inset. We note that at low temperatures the simulation at high fields fails due to numerical issues. We observe that although the chosen model describes the experimental data well at the field range commonly used in other experiments, the fit to the data is rather poor at higher fields. Especially the calculated crossover at 200 MV/m is unrealistic.

As a next step, we turn to a different theoretical description, developed by Vissenberg and Matters (VM), which is based on variable range hopping in an exponential density of states [15]. The model takes into account a charge carrier density dependent mobility, and it has been extensively used to model charge transport in organic

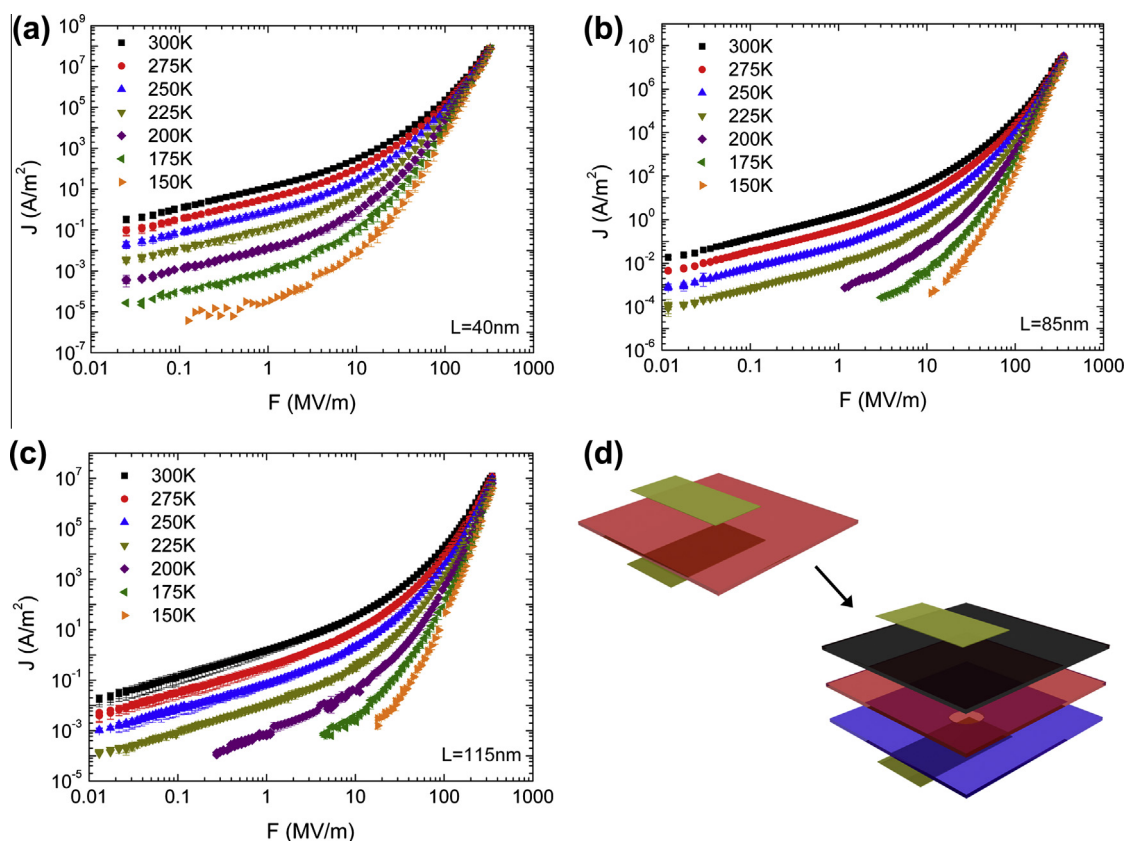


Fig. 2. Current density as a function of applied electric field for MEH-PPV hole-only diodes fabricated in the molecular junction geometry. The MEH-PPV layer thicknesses are (a) 40 nm, (b) 85 nm and (c) 115 nm. (d) Schematic of a standard LED structure and of the molecular junction architecture, in which the extra photo-resist (blue) and PEDOT:PSS (black) layers are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

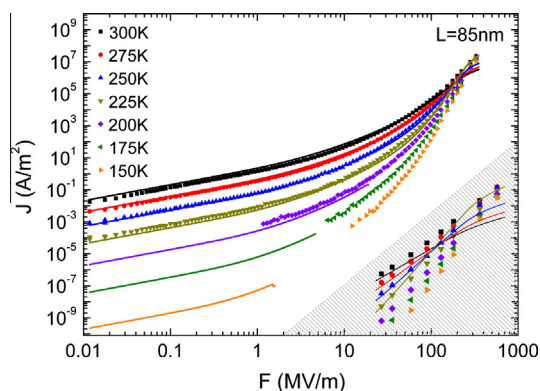


Fig. 3. Current density as a function of applied electric field for an MEH-PPV hole-only diode with a layer thickness of 85 nm at temperatures between 150 K and 300 K. The solid lines are fits to the data using a numerical drift–diffusion model based on the Extended Gaussian Disorder Model. The inset shows a magnification of the crossover at the high field regime.

field-effect transistors (FETs). Since in our SCL diodes similar high densities are obtained as in FETs, also the VM model can be tested. An important difference with FETs is that in our diodes a high voltage induces simultaneously a high electric field next to a high carrier density. Effects of the electric field on the mobility are not included in the VM model, since in organic FETs the electric field along the channel is very low due to the low applied source-drain bias and long channel length. It has been reported [5,6] that at room temperature the mobility is mainly dominated by charge density effects. It was demonstrated that a mobility that is constant at low densities and increases with the VM power law on density for densities $>10^{16} \text{ cm}^{-3}$ can consistently describe the room temperature J – V characteristics of organic hole-only diodes, an eventual field-dependence of the mobility at room temperature was not needed [5]. The advantage of using this empirical mobility was that all VM mobility parameters were measured from a FET, so there were no unknown fitting parameters. With our new device structure we can investigate whether at room temperature the field dependence of the mobility can also be ignored at high voltages. In Fig. 4 we show the room temperature J – V characteristics of the hole-only devices of Fig. 2 together with the calculated J – V (dashed lines) characteristics following the VM transport model. For clarity, only the data for the 40 nm and 85 nm diodes are plotted. We observe that only up to fields of approximately 10 MV/m the VM model gives a consistent description of the charge transport at room temperature, as observed before [5]. Above these fields we have to include a field dependence of the Poole–Frenkel type [16]. The mobility within this model exhibits a field enhancement that depends on the square root of the field exponentially, with a temperature and disorder dependent pre-factor γ [3,17]. We note that Pasveer et al. [6] showed that in the EGDM model the density and field dependence of the mobility can be factorized. Here, by adding the $\exp(\gamma\sqrt{E})$ factor we followed a similar approach. Inclusion of a Poole–Frenkel factor $\exp(\gamma\sqrt{E})$, with a value for γ of $3.5 \times 10^{-4} \text{ (m/V)}^{1/2}$, in the VM model gives a good

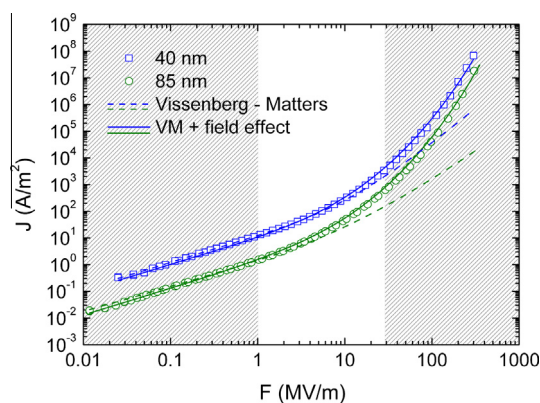


Fig. 4. Current density as a function of applied electric field at room temperature for MEH-PPV hole-only diodes with a layer thickness of 40 nm and 85 nm. The dashed lines are the calculated characteristics following the Vissenberg–Matters transport model. The solid lines represent the calculated current density characteristics when a Poole–Frenkel factor $\exp(\gamma\sqrt{E})$ is included in the VM model.

description of the J – V characteristics in the full field range up to 300 MV/m (solid lines). The value for γ is in good agreement with previous reports [3,17]. We note that such a functional dependence of the mobility on the field cannot describe the convergence of the current density for different temperatures at high fields. Both the EGDM and VM with extended field-dependence models fail in this respect. The development of a charge transport model that consistently describes the charge transport at high electric field is a future challenge.

With the prefactor γ known, we can also disentangle the effects of carrier density and electric field on the charge carrier mobility. Similar to Tanase et al. [5] we extract the mobility as a function of charge carrier density directly from the J – V characteristics, disregarding the field effect. The values derived for MEH-PPV diodes with layer thicknesses of 40 nm, 85 nm and 115 nm are presented as a function of charge carrier density by the open symbols in Fig. 5. Mobility values extracted for conventional MEH-PPV light-emitting diodes and for field-effect transistors by Craciun and Wildeman [18] are included for comparison. The high mobility values extracted in our diodes demonstrate that we have to correct for the field dependence, $e^{2\gamma\sqrt{F}}$, as obtained from Fig. 4. The solid symbols then represent the corrected, low field, mobility values. A good agreement with the data reported previously by Craciun and Wildeman [18] is obtained. We observe that the gap between LEDs and FETs can be bridged without having to resolve exclusively to thin or doped polymer layers, as previously reported [18,19]. In contrast to these studies, the charge carrier density values in our devices do not simply approach, but overlap well with those achieved in a field-effect transistor. A unified description is obtained.

4. Extracting the hopping length

The convergence of the current density data at high electric fields (Fig. 2 and inset of Fig. 3) can be used to extract directly from the experimental data a basic parameter

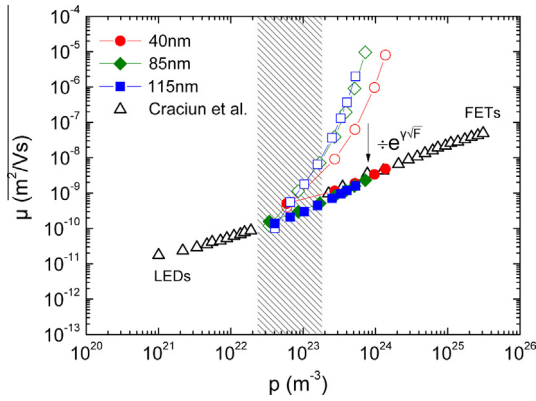


Fig. 5. Mobility, μ , as a function of charge carrier density, p , extracted from MEH-PPV diodes with layer thicknesses of 40 nm, 85 nm and 115 nm (open symbols). Mobility values for MEH-PPV light-emitting diodes and field-effect transistors derived by Craciun and Wildeman [18] are included for comparison (Δ). The solid symbols represent mobility values after correction for the field dependence, $e^{7/\sqrt{F}}$. The charge carrier density was extracted in each case from the middle of the MEH-PPV layer, at different applied fields.

of hopping transport, viz. the hopping length. A sufficiently large applied field is a strong perturbation to the thermal, diffusive motion of charge carriers. In a first order approximation, the J - V characteristics for different temperatures converge once the energy provided by the electric field can overcome the activation energy of the sequential hops between the localized sites in the polymer. The convergence field can then be used to estimate an average hopping length for the material. Using the approximation:

$$F_c \ell_{hop} = E_a \quad (1)$$

where F_c is the convergence field, ℓ_{hop} is the hopping length and E_a is the activation energy, one obtains the following relation between the convergence bias, V_c , and the thickness, L , of the polymer film in the diode:

$$V_c = E_a L / \ell_{hop} \quad (2)$$

From the current density–electric field characteristics of Fig. 2, the convergence field, at which the current density

is independent of temperature, can be determined. We use a simple power-law extrapolation, as depicted in Fig. 6a for the case of the diode with an 85 nm thick MEH-PPV layer. In Fig. 6b the convergence voltages are presented as a function of film thickness. A linear dependence in agreement with Eq. (2) is obtained. The slope is given by E_a/ℓ_{hop} . Taking an activation energy for MEH-PPV of 0.45 eV [18,20], we find an average hopping length ℓ_{hop} of 1.0 ± 0.1 nm. This value is in good agreement with hopping distances as reported for PPV-type semiconductors [21].

5. Summary and conclusions

We have used the experimental testbed of molecular junctions to characterize charge transport in MEH-PPV-based hole-only diodes over an unprecedented range of electric field and temperature. The data set presented here can be used as a benchmark to verify any theoretical charge transport model. We demonstrate that the commonly used transport model, viz. the Extended Gaussian Disorder Model, describes the experimental data well only in the field range that is conventionally used in experiments. The fit to the data is rather poor at higher fields. Similarly, the Vissenberg-Matters transport model consistently describes the charge transport at room temperature up to fields of approximately 10 MV/m. Above these fields we have to include a Poole–Frenkel type field dependence, $\exp(\gamma\sqrt{E})$, where the pre-factor γ depends on temperature and disorder. With the prefactor γ extracted at room temperature, we have disentangled the effects of carrier density and electric field on the charge carrier mobility. The gap between conventional LEDs and FETs has been bridged. However, the convergence of the current density for different temperatures at high fields is correctly described by neither the EGDM nor the VM with extended field-dependence. The development of a charge transport model that consistently describes the charge transport at high electric field is a future challenge.

The convergence of the current density at high fields enables us to quantify the energy provided by the electric field to overcome the activation energy of the sequential

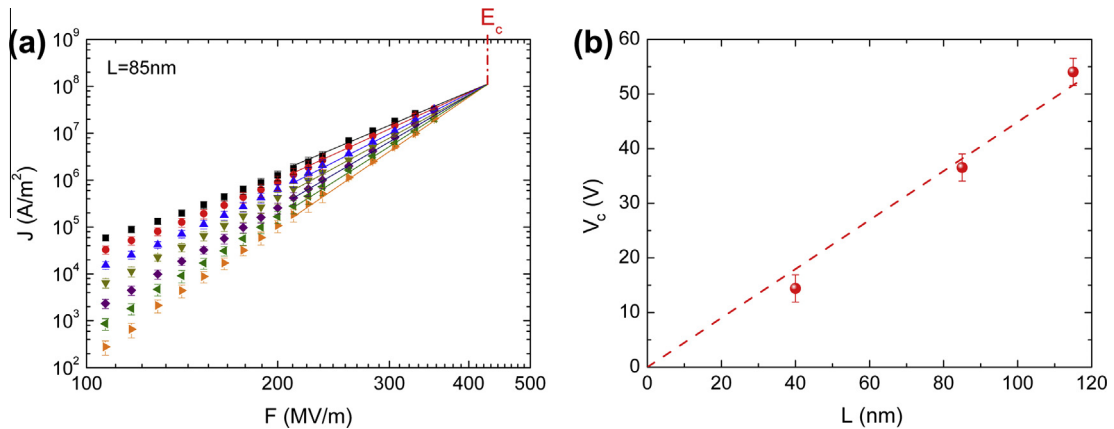


Fig. 6. (a) Magnification of the high field regime for the current density versus electric field as a function of temperature of an MEH-PPV hole-only diode with a layer thickness of 85 nm. Solid lines represent a power-law extrapolation to estimate the convergence field, F_c . (b) Convergence voltage as a function of layer thickness for MEH-PPV hole-only diodes as a function of layer thickness. The dashed line is the linear fit to the data.

hops between the localized sites in the polymer. With a simple approximation, we have extracted directly from the experimental data at high fields a hopping length of 1.0 ± 0.1 nm for holes in MEH-PPV.

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